

The Condensation of Carbon Tetrachloride and Phenol:Aurin

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE
UNIVERSITY OF MICHIGAN

By

Harold Robert Snow

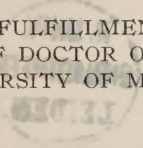
EASTON, PA.
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CONTENTS

I	Introduction.....	5
II	The Mechanism of the Condensation Reaction.....	5
III	The Separation of the Reaction Mixture into its Components.....	6
IV	The Relative Proportion of the Components.....	8
V	The Preparation of Diphenyl Carbonate.....	8
VI	The Preparation of Di- <i>p</i> -hydroxybenzophenone.....	9
VII	Aurin.....	9
	Preparation.....	9
	Combination with Solvents of Crystallization.....	10
	The Possible Existence of the Quinoid Carbinol of Aurin.....	11
	Tri-Acetyl-Aurin.....	12
	Tri-Acetyl-Aurin Chloride.....	12
	Tri-Acetyl-Aurin Peroxide.....	12
	Tribenzoyl-Aurin.....	13
	Tribenzoyl-Aurin Chloride.....	13
	Tribenzoyl-Aurin Peroxide.....	13
	Decomposition of Aurin by Air and Alkali.....	14
	Isolation of Leuco Aurin from the Condensation Product.....	14
VIII	<i>o,p',p''</i> -Trihydroxy-Triphenyl Carbinol.....	14
	Isolation from the Condensation Mixture.....	14
	Preparation of <i>o,p',p''</i> -Trimethoxy-triphenyl Carbinol, by the Grignard Reaction.....	14
	<i>o,p',p''</i> -Trimethoxy-triphenylmethane.....	15
IX	<i>p</i> -Hydroxyphenyl-Xanthane.....	15
	<i>p</i> -Methoxyphenyl-Xanthane.....	15
X	<i>p</i> -Hydroxyphenyl-Fluorone.....	15
	Isolation from the Condensation Product.....	15
	<i>p</i> -Acetoxyphenyl-Fluorone.....	15
	<i>p</i> -Acetoxyphenyl-3-Acetoxy-Xanthenol.....	15
	<i>p</i> -Methoxyphenyl-Fluorone.....	16
	<i>p</i> -Methoxyphenyl-3-Methoxy-Xanthenol.....	16
	Synthesis of <i>p</i> -Hydroxyphenyl-Fluorone.....	16
	Oxidation by Air and Alkali.....	16
XI	The Oxalic Acid Method for the Preparation of Aurin.....	17
XII	The Composition of Several Technical Samples of Aurin.....	17
XIII	Summary.....	18

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THE CONDENSATION OF CARBON TETRACHLORIDE AND PHENOL: AURIN

Friedel,¹ in a note, states that aurin is formed when carbon tetrachloride is heated with an excess of phenol and zinc chloride. Heumann² patented a process for producing aurin by heating under pressure carbon tetrachloride and phenol with various condensing agents, such as aluminum chloride, stannic chloride or zinc chloride and he stated that without pressure, only a trace of aurin is produced.

We have investigated this reaction and find that Heumann's assertion is incorrect. Aurin is produced in quite as good yield when the condensation is carried on at ordinary pressure as when in an autoclave, namely, about 35%. We find also that many other products are formed simultaneously with aurin. The successful isolation of certain intermediate products, together with the identification of all the final products, has enabled us to give an interpretation as to the probable mechanism of this condensation reaction.

We have also studied the method for making aurin which has been commonly used in the past, namely, from phenol, oxalic acid and sulfuric acid, and we find that here, too, a mixture of various substances results, and that the technical product is far from pure aurin.

The Mechanism of the Condensation Reaction

1. The first stage in the reaction consists in the condensation of two molecules of phenol with one of carbon tetrachloride and diphenoxy-dichloromethane (I) is thus formed.³ If the requisite amount of water be present in the mixture, this dichloride becomes hydrolyzed to diphenyl carbonate (II), which is stable and can undergo no further change under the conditions of the experiment. In fact, good yields of diphenyl carbonate can be obtained by this method.

¹ Friedel, *Bull. soc. chim.*, **50**, 2 (1888).

² Heumann, *Friedländer*, **3**, 103; Ger. pat., 68,976, 1893.

³ Gomberg and Jickling, *J. Am. Chem. Soc.*, **37**, 2580 (1915).

2. However, if the diphenoxy-dichloride does not become hydrolyzed as soon as formed, then, due to the influence of the hydrogen chloride present, it undergoes an intramolecular rearrangement and gives rise to di-*p*-hydroxybenzophenone chloride (III), and to a small amount of the isomeric *o*,-*p*'-dihydroxy derivative (V). Hydrolysis of the reaction mixture at this stage gives rise to the two ketones (IV) and (VI). This constitutes a very excellent method for the preparation of *p*,*p*'-dihydroxybenzophenone.

3. If the ketones are not the desired end-products of the condensation, then hydrolysis of the keto chlorides should be carefully avoided. The two keto chlorides described above now condense further with a third molecule of phenol, and there are produced the chlorides of the three possible triarylcarbinols: *p*,*p*',*p*''-trihydroxy-triphenyl carbinol (VII), and the two isomers thereof: *o*,*p*',*p*'' (IX) and *o*,*o*', *p*'' (XI). Product VII is the precursor of aurin (VIII). Similarly, Substance IX gives rise to the anhydride of *o*,*p*',*p*''-trihydroxy-triphenyl carbinol (X), while Compound XI of course loses spontaneously a molecule of water from the two *o*-hydroxyl groups, whereby a xanthone ring becomes established in the molecule, and there is thus produced the chloride of *p*-hydroxyphenyl-xanthenol (XII).

4. Substance IX, however, in addition to its normal change into X, undergoes in part still another change. It, too, goes over into a xanthone derivative. Here, however, the new ring is established through the loss not of a molecule of water, but of two atoms of hydrogen—the one from the *o*-hydroxyl group and the second from a CH group in the *ortho* position in one of the other two benzene rings. There is thus produced the unstable compound (XIII), which is the precursor of *p*-hydroxyphenyl-fluorone (XIV). A similar tendency on the part of hydroxytriaryl carbinols to establish a xanthone ring within the molecule, through dehydrogenation, has been observed in other cases.⁴

5. The nascent hydrogen which originates as described in the preceding paragraph, reacts with the triarylcarbinol chlorides or the carbinols themselves. Apparently under the conditions of our experiments Substances VII and XII are the two most susceptible to reduction and there are thus produced the two corresponding leuco derivatives, namely, leuco-aurin (XV) and *p*-hydroxyphenyl-xanthane (XVI).

The Separation of the Reaction Mixture into its Components

Since the products formed, with the exception of diphenyl carbonate, contain phenolic hydroxyl groups, they possess acid properties, the degree of acidity depending upon the number of hydroxyl groups in the molecule, as well as upon the configuration of the latter. Consequently, the constituents may be divided into two main groups: (1) products soluble

⁴ Baeyer, *Ann.*, 354, 170 (1907).

in very dilute ammonium hydroxide solution (1.5%); (2) products insoluble in ammonium hydroxide of that dilution. The basis for further separation is briefly indicated in the following outline.

1. Products soluble in dil. ammonium hydroxide: (a) aurin (insoluble in ether); (b) di-*p*-hydroxybenzophenone (soluble in ether, slightly soluble in hot benzene); (c) *o,p'*-dihydroxybenzophenone (soluble in ether, soluble in hot benzene).

2. Products insoluble in dil. ammonium hydroxide: (d) *p*-hydroxyphenyl-fluorone (XIV) (insoluble in moist ether, in contradistinction to all those below, all of which are soluble in ether); (e) the *o,p',p''*-trihydroxy compound (X) (upon passing hydrogen chloride into the ether solution it forms an insoluble chloride-hydrochloride,⁵ and is thus separated from those mentioned below, all of which remain in solution); (f) leuco-aurin (XV) (soluble, together with a small amount of unidentified substances (Z), in cold dil. sodium hydroxide solution); (g) *p*-hydroxyphenyl-xanthane (XVI) (the sodium salt is insoluble in cold, but soluble in hot dil. sodium hydroxide solution); (h) diphenyl carbonate (not soluble in either cold or hot alkali); (i) (Z) unidentified substance (small amount).

The Relative Proportions of the Components

When the relative proportions of carbon tetrachloride and phenol are nearly those calculated on the basis of the equation, one molecular equivalent of the former to 3.5 of the latter, and when all moisture is carefully excluded, then the amount of aurin is usually 32% to 35% of that calculated, and it constitutes about 55% in weight of all the condensation products. The data following are the averages of ten carefully conducted experiments, using each time 154 g. of carbon tetrachloride, 330 g. of phenol and 50 g. of zinc chloride: aurin, 90–94 g.; *p*-hydroxyphenyl-fluorone, 25 g.; *o,p',p''*-trihydroxytriphenyl carbinol, 15 g.; leuco-aurin, 20 g.; *p*-hydroxyphenyl-xanthane, 7 g.; ketones, very small amount; diphenyl carbonate, trace.

Experimental Part

The Preparation of Diphenyl Carbonate

Diphenyl carbonate has usually been prepared by methods which require the use of carbonyl chloride and such methods present obvious disadvantages. Very satisfactory yields of this ester were obtained as follows.

To 94 g. (1 mole) of phenol in a flask were added 10 g. of zinc chloride, 95 g. (0.55 mole) of carbon tetrachloride and 41 g. (0.5 mole) of zinc oxide and the mixture was heated under a reflux condenser at 120° until no further evolution of hydrogen chloride was noticed. This required about 24 hours. The small amount of zinc chloride served to start the reaction; thereafter, the hydrogen chloride produced in the course of the reaction, combining with the zinc oxide, formed additional zinc chloride and this reaction also furnished the water requisite for the hydrolysis of the diphenoxy-dichloromethane to the carbonate. The excess of carbon tetrachloride and unchanged phenol

⁵ Gomberg and Cone, *Ann.*, 370, 191 (1909).

were removed by steam distillation, the distillation being continued until the carbonate commenced to distil. The viscous mass was poured into a large volume of water while the latter was vigorously stirred. After the product had been washed several times by decantation, the insoluble residue was digested with 5% sodium hydroxide solution, in order to dissolve the hydroxybenzophenones and the small amount of dye present. The carbonate remained as a white crystalline substance, contaminated with a small amount of zinc salts. It was purified by recrystallization from alcohol; yield, 45 g., or 50%, calculated on the basis of the phenol used.⁶

On passing sulfur dioxide into the alkaline wash solution, 25 g. of crude dihydroxybenzophenones was obtained.

The Preparation of Di-*p*-hydroxybenzophenone

The procedure was very similar to that used in the preparation of diphenyl carbonate, except that an increased amount of freshly molten zinc chloride (50 g.) was used at the start and no zinc oxide was added.

The mixture of the ketones was isolated in the same manner as indicated under the preparation of diphenyl carbonate. The crude product was then dissolved in dil. ammonium hydroxide, the solution filtered, warmed and treated with sulfur dioxide, whereupon the ketones separated as almost colorless needles; 33 g. of the mixed ketones and only a small amount of carbonate were obtained from 94 g. of phenol, equal to a 36% yield based on the phenol used.

The mixture consists largely of *p,p'*-dihydroxy ketone and contains only a small amount of the isomeric *o,p'*-compound. The latter is far more soluble in hot benzene than the former, and may thus be readily removed.

Aurin, (4,4'-Dihydroxy-diphenylquinomethane VIII)

Preparation.—After many trials the following procedure was finally adopted.

Three hundred and thirty g. (3.5 moles) of pure phenol was placed in a flask that could be connected to a reflux condenser by means of a ground-glass joint (if a cork must be used it should be covered with lead foil). The phenol was melted and into it 50 g. of molten zinc chloride was poured while the flask was given a rotary motion so as to distribute the zinc chloride in the form of fine threads through the solution. The mixture, carefully protected from moisture, was heated in an oil-bath for 18 hours at 135°, with the gradual addition of 154 g. (1 mole) of carbon tetrachloride. The viscous mass was steam-distilled, in order to remove the excess of phenol. It was then poured very slowly into 2 liters of vigorously stirred water containing 60 cc. of hydrochloric acid. After filtering and washing the material thoroughly with water, it was extracted with 1.5% ammonium hydroxide. In ammonium hydroxide of this concentration, aurin and the hydroxybenzophenones are dissolved, while the other products (see scheme on p. 8) are almost entirely insoluble. The ammoniacal filtrate was heated to 70–80° and the aurin, with the small amount of ketones, was precipitated by adding dil. acetic acid (not hydrochloric acid, see p. 11) slowly and vigorously stirring the mixture. The product separated either as a brick-red powder or as purplish-red crystals, depending mainly upon the temperature of the solution and the rate with which the acid was added. The precipitate was filtered and washed with water containing a little acetic acid and finally with water. In order to remove any ketones

⁶ Dr. H. T. Clarke of the Eastman Kodak Co. has been good enough to test this method on a larger scale. From 1200 g. of phenol, heated at 100–110° for 15 hours and stirred, 437 g. of pure vacuum-distilled diphenyl carbonate was obtained.

present, the dry product was first stirred with ether and then allowed to stand overnight, whereupon the ketones dissolved. When the ether is moist the aurin changes to a crystalline product with steel-blue luster, and takes up ether of crystallization. The aurin is now very pure and for most purposes need not be further purified. The yield is from 95 to 100 g., or 33%, based upon the carbon tetrachloride used. After recrystallization from glacial acetic acid, the substance melts at 295–300° with the evolution of phenol.

Anal. Calcd. for $C_{19}H_{14}O_3$: C, 78.59; H, 4.86. Found: C, 78.20; H, 4.94.

Pure aurin changes from yellow to red between P_H 5.6 and 6.5.

Combination with Solvents of Crystallization.—Aurin is soluble to the extent of about 2 g. in 100 cc. of boiling glacial acetic acid and crystallizes from the solution in garnet-red crystals. When benzene is added to a cold, saturated solution of aurin in glacial acetic acid, the dye precipitates on long standing in large, heavy, needle-like crystals with steel-blue reflection, which carry acetic acid and benzene. In acetic acid, varying in concentration from 80% to 95%, aurin is soluble to the extent of about 4 g. in 100 cc. at the boiling temperature. It crystallizes from this solution on long standing, carrying acetic acid and water. Aurin is soluble with difficulty in acetone and in methylethyl ketone and it crystallizes from these, carrying solvent of crystallization. As previously mentioned, aurin takes up ether of crystallization when suspended in the moist solvent.

The compositions of these combinations have been found to be as follows: from acetic acid and benzene, $2(C_{19}H_{14}O_3) \cdot 2(C_2H_4O_2) \cdot C_6H_6$; from acetic acid and water, $C_{19}H_{14}O_3 \cdot 1\frac{1}{2}(C_2H_4O_2) \cdot H_2O$; from acetone, $2(C_{19}H_{14}O_3) \cdot 3(C_3H_6O)$; from methylethyl ketone, $C_{19}H_{14}O_3 \cdot C_4H_8O$; from ether, $C_{19}H_{14}O_3 \cdot C_4H_{10}O$.

AURIN HYDROCHLORIDE.—Dale and Schorlemmer⁷ have noted the tendency of aurin to unite with acids and have described a crystalline product of aurin with one molecule of hydrogen chloride. This property of fuchsones to unite with hydrogen chloride is well known, and is interpreted by some as formation of oxonium and by others as that of quinocarbonium salts. Gomberg⁸ assigned to the addition product of hydrogen chlor-

ide with aurin the constitution $(HOC_6H_4)_2 = C = \text{C}_6\text{H}_3\text{Cl}_2\text{OH}$.

We found that when aurin is crystallized from alcohol saturated with hydrogen chloride, the hydrochloride precipitated with one molecule of alcohol of crystallization, and not in the ratio of two molecules of the former to three of the latter, as described by Dale and Schorlemmer.

Anal. Calcd. for $C_{19}H_{15}O_3Cl \cdot C_2H_6O$: C_2H_6O , 12.35. Found: 12.3.

The compound prepared in acetic acid as the solvent contains two molecules of acetic acid of crystallization, which is readily driven out when the salt is heated at 100°.

Anal. Calcd. for $C_{19}H_{15}O_3Cl$: HCl, 11.8. Found: 11.5.

Aurin was recrystallized from hot, dil. hydrochloric acid (1:1). It precipitated in

⁷ Dale and Schorlemmer, *J. Chem. Soc.*, **35**, 154 (1879).

⁸ Gomberg and Cone, *Ann.*, **376**, 213 (1910).

fine, brown needles; these were washed with a few cubic centimeters of water, pressed on a porous plate, allowed to stand for 24 hours, powdered and air-dried for several hours. When heated to constant weight at 120°, the substance lost 10.7% of water, while only a trace of hydrogen chloride was given off. The composition of the hydrate is, $C_{19}H_{16}O_3 \cdot Cl_2 \cdot 2H_2O$.

When aurin is placed even in dilute solutions of hydrochloric acid, it forms an additive product with the acid; for this reason hydrochloric acid must be avoided in precipitating aurin from its alkaline solutions. The avidity with which aurin unites with hydrogen chloride in dilute aqueous solutions is shown by the following experiment. Two g. of pure aurin was kept at 50° with 50 cc. of 2% hydrochloric acid. The garnet-red crystals of aurin soon turned to brown threads and the product consisted almost entirely of the hydrated aurin hydrochloride.

The Possible Existence of the Quinoid Carbinol of Aurin,



In previous publications from this Laboratory it has been shown that *p*-hydroxy-triaryl carbinols exhibit the phenomenon of tautomerism.



A detailed study of aurin has now shown that it, too, in all probability exists not only as the well-known anhydride, the fuchsone, but also as an unstable carbinol. The equilibrium, however, in this instance is wholly in favor of the quinoid tautomer, which is not surprising, in view of the three hydroxyl groups in the molecule. We have prepared a compound corresponding in composition to the carbinol plus one molecule of water of crystallization. From a consideration of the following points it appears that we have here not a dihydrate of aurin but actually a monohydrate of the carbinol: (1) there is a decided change in color of the carbinol from that of the fuchsone aurin; (2) aurin hydrochloride, which possesses a constitution similar to our surmised carbinol, also contains water of crystallization; (3) one molecule of water in our carbinol plays a different role from the other, the first being given off more readily than the second.

Ordinarily, from its solutions in alkalis, aurin is precipitated as the fuchsone, whether the alkali be dilute or concentrated, cold or hot, whether the precipitation be accomplished by just neutralizing with acetic acid, or adding an excess of the latter, or whether the dye be precipitated by passing carbon dioxide into the solution. When hydrochloric acid is used, then if the amount of acid added is just enough to neutralize the alkali, fuchsone is the result; when a considerable excess of acid is added, the fuchsone is contaminated with some fuchsone hydrochloride. We have finally succeeded in getting the desired hydrated carbinol by observing the following conditions. Aurin is dissolved in sodium hydroxide and to the warm solution (60° to 70°) is slowly added dilute (1:4) hydrochloric acid, while the solution is well stirred. At the neutral point, the

precipitate consists of light red fuchson, but when a slight excess of acid is added and the stirring of the warm solution is continued for 15 minutes, the red fuchson soon turns to fine purple threads consisting almost entirely of hydrated aurin. A sample of such a product was dried on a porous plate for 24 hours, powdered and air-dried for several hours longer. A weighed amount of the substance was then dehydrated by passing over the sample in a porcelain boat dry air at room temperature and finally heating to 100°. A gradual loss of water occurred—1 mol. in the first ten hours, 0.8 mol. in the next 40 hours, and evidently approaching asymptotically 1.95 molecule of water.

The slight excess of hydrochloric acid over that necessary for the neutralization of the alkali in the preparation of aurin hydrate probably forms a correspondingly small amount of aurin hydrochloride. This gradually becomes hydrolyzed to aurin hydroxide and the liberated acid continues to act in the same manner as before until all of the aurin is changed to the carbinol. In confirmation of this interpretation we may cite the fact that pure aurin hydrochloride when suspended in water is transformed to the extent of 50% to the hydrated fuchson. On prolonged standing, especially at low temperature, fuchson is the product.

Tri-acetyl-aurin (Tri-*p*-acetoxy-triphenylcarbinol), $(\text{CH}_3\text{COOC}_6\text{H}_4)_3\text{COH}$.—Ten g. of aurin, 50 cc. of acetic anhydride and 2 g. of anhydrous sodium acetate were boiled under a reflux condenser for two hours. The yield of the crude product was 14 g., that is, almost quantitative. One recrystallization from alcohol gave 13 g. of a colorless crystalline product; m. p., 170–172°. The pure compound melts at 172–173°. ⁹

Herzig¹⁰ describes two compounds from the reaction between acetic anhydride and aurin, one insoluble in alcohol, melting at 172°; the other, a more soluble product, melting at 146–148°. His results could not be verified; a single product with a definite melting point of 172–173° was obtained by us.

TRI-ACETYL-AURIN CHLORIDE (TRI-*p*-ACETOXYTRIPHENYL-CHLOROMETHANE), $(\text{CH}_3\text{COOC}_6\text{H}_4)_3\text{CCl}$.—To a solution of 15 g. of acetyl aurin in 10 cc. of hot benzene is added 8 cc. of acetyl chloride. The solution soon turns pink and on longer standing the chloride separates in well-formed, slightly colored crystals which carry benzene of crystallization in the ratio of one molecule of benzene to one molecule of the chloride. When the compound is digested with absolute ether, it still retains most of the benzene. The chloride can, however, be obtained free from solvent when the fine crystalline product is heated at 78°, under reduced pressure, in a stream of air dried over phosphorus pentoxide. The compound turns yellow when heated, begins to soften at 168° and melts at 174° to a red liquid with the evolution of acetyl chloride.

Anal. Calcd. for $\text{C}_{25}\text{H}_{21}\text{O}_6\text{Cl}$: Cl, 7.84. Found: 7.76.

The chloride begins to give off acetyl chloride at 120°, more rapidly at 160°, until one molecule of acetyl chloride has been lost. The product left is undoubtedly diacetyl-aurin, $(\text{CH}_3\text{COOC}_6\text{H}_4)_2\text{C}:\text{C}_6\text{H}_4:\text{O}$.

TRI-ACETYL-AURIN PEROXIDE (TRI-*p*-ACETOXYTRIPHENYL-METHYL PEROXIDE), $(\text{CH}_3\text{COOC}_6\text{H}_4)_3\text{C}.\text{O}.\text{O}.\text{C}(\text{C}_6\text{H}_4\text{OOCCH}_3)_3$.—By the action of molecular silver upon the

⁹ (a) Graebe and Caro, *Ber.*, **11**, 1122 (1878). (b) Dale and Schorlemmer, *Ann.*, **196**, 84 (1879). (c) Zulkowsky, *Ann.*, **202**, 191 (1880).

¹⁰ Herzig, *Monatsh.*, **17**, 191 (1896).

chloride, tri-*p*-acetoxytriphenylmethyl should result. This free radical is very unstable and was not isolated. The fact of its transitory existence was established by the isolation of the corresponding peroxide. Quantitative determinations of the amount of oxygen that is absorbed by the free radical were made by sealing the chloride and silver with a solvent, in a test-tube, shaking at room temperature for a definite time, and then measuring the amount of oxygen that the solution absorbs. Results were obtained indicating an absorption from 15 to 35% of that calculated, and then only a small amount of the peroxide could be isolated from the solution—thus indicating the progressive decomposition of the radical; but by shaking a bromobenzene solution of the chloride with silver directly in the absorption apparatus in the presence of oxygen, amounts of absorption were obtained varying from 99% to 103% of that calculated, and then the yields of peroxide were 80 to 85%. The peroxide was recrystallized from methylethyl ketone. It melts at 184–185° to a red liquid.

Anal. Calcd. for $C_{60}H_{42}O_{14}$: C, 69.27; H, 4.88. Found: C, 69.25; H, 4.88.

Tribenzoyl-aurin (Tri-*p*-benzoxytriphenylcarbinol), $(C_6H_5COOC_6H_4)_3COH$.—To 10 g. of aurin suspended in 25 cc. of dimethylaniline was added slowly 25 g. of benzoyl chloride and the solution was finally heated to 60° for one hour. The resulting mixture was washed first with dil. hydrochloric acid and then with sodium hydroxide. The yield after one recrystallization of the crude material from benzene was 13 g. of pure white product. The compound melts at 190–191°.

Anal. Calcd. for $C_{40}H_{28}O_7$: C, 77.40; H, 4.55. Found: C, 77.24; H, 4.44.

This substance surpasses even aurin itself in the singular property of combining generally with solvents from which it is crystallized. It is difficult to find an explanation why this carbinol, structurally saturated, should possess even more residual affinity than aurin, which is structurally unsaturated. The following combinations have been obtained.

Solvent	Product	Solvent	Product
Benzene	$2 C_{40}H_{28}O_7 \cdot 3 C_6H_6$	Acetone	$C_{40}H_{28}O_7 \cdot C_3H_6O$
Acetic acid	$C_{40}H_{28}O_7 \cdot C_2H_4O_2$	Methylethyl ketone	$2 C_{40}H_{28}O_7 \cdot CH_3COC_2H_5$
Alcohol	$C_{40}H_{28}O_7 \cdot C_2H_6O$	Methylpropyl ketone	$2 C_{40}H_{28}O_7 \cdot CH_3COC_3H_7$
Carbon tetrachloride	$C_{40}H_{28}O_7 \cdot CCl_4$		

TRIBENZOYL-AURIN CHLORIDE (TRI-*p*-BENZOXYTRIPHENYL-CHLOROMETHANE), $(C_6H_5COOC_6H_4)_3CCl$.—To a solution of 10 g. of tribenzoyl aurin in 75 cc. of warm benzene was added calcium chloride and the solution saturated with dry hydrogen chloride. After several hours the mixture was warmed gently in order to bring into solution the carbinol chloride which had precipitated, and the calcium chloride was filtered off. The solution was concentrated and absolute ether added. The chloride precipitated in white crystals carrying benzene of crystallization, 1 molecule of the solvent to 1 of the chloride. It loses the solvent of crystallization when heated to temperatures slightly above the boiling point of benzene and melts at 172–174° to a red liquid.

Anal. Calcd. for $C_{40}H_{27}O_6Cl$: Cl, 5.56. Found: 5.47.

TRIBENZOYL-AURIN PEROXIDE (TRI-*p*-BENZOXYTRIPHENYL-METHYL PEROXIDE), $(C_6H_5CO \cdot OC_6H_4)_3C \cdot O \cdot O \cdot C(C_6H_4O \cdot OCC_6H_5)_3$.—As in the case of the acetyl compound, it is necessary to prepare this peroxide by the simultaneous action of silver and oxygen upon the chloride in solution; otherwise, the radical decomposes to a large extent prior to the oxidation process. By the simultaneous action of silver and oxygen upon the solution of the chloride, absorptions of oxygen were obtained varying from 100% to 103% of that calculated. The solution of the peroxide was evaporated to a small volume, and the resulting yellow oil was treated with ether which dissolved the im-

purities, while the peroxide separated as colorless crystals; yield, 68%. When crystallized from chloroform it carries solvent of crystallization which it retains very firmly. After drying at 100° the compound when further heated melts at 218° to a red liquid.

Anal. Calcd. for $C_{80}H_{64}O_{14} \cdot 4CHCl_3$: C, 77.54; H, 4.39; $CHCl_3$, 27.85. Found: C, 77.12, 77.06; H, 4.34, 4.53; $CHCl_3$, 27.3.

Decomposition of Aurin by Air and Alkali.—Aurin can be oxidized by atmospheric oxygen in the presence of alkalis with much greater ease than has been usually assumed. Fusion is not necessary.¹¹ Ten g. of aurin was dissolved in 200 cc. of 5% sodium hydroxide and air was passed through the cold solution for 72 hours. The filtered solution gave, on the addition of acetic acid, 5.8 g. of pure di-*p*-hydroxybenzophenone.

Isolation of Leuco-aurin from the Condensation Product.—The origin of this product in the reaction mixture has been explained on p. 6 under Section 5. It is to be found in the ether extract of that fraction of the mixture which is insoluble in dil. ammonium hydroxide. The moist ether extract is saturated with hydrogen chloride, decanted from the resulting precipitate and evaporated to dryness. The residue obtained on the evaporation of ether consists of leuco-aurin mixed with a small amount of substance (Z) which still remains unidentified. The leuco compound is purified by recrystallization from chloroform and benzene, in which mixture the product (Z) is more soluble than the former.

The leuco compound was identified by analysis and by a comparison of it with leuco-aurin which was prepared directly from pure aurin by reduction with zinc dust and acetic acid.¹² Each sample softened at 235° and melted at 240°. Furthermore, each of the two samples was acetylated, and they gave the identical triacetyl-leuco-aurin,¹³ m. p., 135–137°.

o,p'p''-Trihydroxy-triphenyl Carbinol (X)

Isolation from the Condensation Mixture.—As mentioned in the preceding paragraph, this compound is to be found together with leuco-aurin. When the ether extract that contains these two substances is saturated with hydrogen chloride, the *o, p', p''*-trihydroxy carbinol forms an insoluble carbinol-chloride, which on treatment with alkali gives the carbinol, or its anhydride the fuchsone. This, however, contains some impurity which is not easily separated. Freshly precipitated, the almost colorless carbinol changes rapidly to a red powder which is soluble in ether; when the product is dried, it is rendered insoluble in ether. We have failed to obtain the carbinol in crystalline form to be identified directly as such. Methylation, benzylation and acetylation also failed to give rise to products that could be crystallized. We then reduced our crude carbinol with zinc and acetic acid to the corresponding leuco base, and after preliminary purification of it from benzene and petroleum ether, we methylated it by means of dimethyl sulfate. The resulting substance, m. p. 113–114°, proved identical with *o,p',p''*-trimethoxy-triphenylmethane which was prepared from its corresponding carbinol that had been synthesized by the Grignard reaction.

Preparation of *o,p',p''*-Trimethoxy-triphenyl Carbinol by the Grignard Reaction.—The Grignard reagent was prepared from *o*-iodo-anisole in ether. Di-*p*-methoxybenzophenone was then added and after the mixture had been boiled for a short time, benzene was added, the ether distilled and the boiling continued. The insoluble magnesium compound of the carbinol was filtered off, washed with benzene, and decomposed

¹¹ (a) Caro and Graebe, *Ber.*, **11**, 1348 (1878). (b) Dale and Schorlemmer, *Ann.*, **217**, 388 (1883). (c) Baeyer and Burkhart, *Ann.*, **202**, 126 (1880).

¹² Dale and Schorlemmer, *J. Chem. Soc.*, **26**, 439 (1873).

¹³ (a) Ref. 9 a, p. 1117. (b) Herzog and Smoluchowski, *Monatsh.*, **15**, 80 (1894).

in the usual manner. The carbinol, recrystallized from benzene and petroleum ether, melted at 124–125°.

o,p',p''-Trimethoxy-triphenylmethane.—This was prepared from the carbinol described by reduction with zinc dust at 80°. The product was recrystallized from petroleum ether. It melted, like the methane from the carbinol in the condensation mixture, at 113–114°. A mixture of the two methane samples, which came from the two different sources, also melted at 113–114°.

p-Hydroxyphenyl-xanthane (XVI)

This product, in the scheme employed for the separation of reaction products, comes in the fraction together with diphenyl carbonate; both are soluble in ether and insoluble in cold dil. sodium hydroxide solution; the latter, however, does not react with alkali, while the former gives a sodium salt that is insoluble in cold, but soluble in hot alkali. The separation of the two is therefore readily accomplished. The xanthane was recrystallized from ether and petroleum ether and melted at 148° to 150° with decomposition.

Anal. Calcd. for $C_{19}H_{14}O_2$: C, 83.19; H, 5.15. Found: C, 83.18; H, 5.17.

p-Methoxyphenyl-xanthane.—For further identification our hydroxy-xanthane was methylated by means of dimethyl sulfate and the methoxy derivative compared with *p*-methoxyphenyl-xanthane obtained directly from the corresponding xanthenol¹⁴ by reduction with zinc dust. The two proved identical, each sample of the xanthane melting at 112–113°.

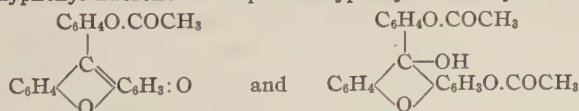
p-Hydroxyphenyl-fluorone (XIV)

Isolation.—This product constitutes about 15% of the whole reaction mixture and, in weight, equals one-fourth of the aurin. Unlike the latter, it is not soluble in dil. ammonium hydroxide, as it is a weaker acid, containing only one phenolic hydroxyl group while aurin contains two. It is separated from other products as indicated on p. 8. The crude fluorone is now washed with 50% acetone, which removes small amounts present of *o,p',p''*-trihydroxy-carbinol (X) and of a greenish-black substance, that otherwise interfere with the crystallization of the fluorone. After this treatment the product is a light orange powder and is quite pure. It gives with alkali a red color bordering on orange, while aurin gives a pure red solution. The fluorone is insoluble in the usual organic solvents except acetic acid, from which it crystallizes in orange-red crystals. It melts at 285–295° with the evolution of phenol.

Anal. Calcd. for $C_{19}H_{12}O_3$: C, 79.14; H, 4.20. Found: C, 78.80; H, 4.31.

The constitution of the compound described above as *p*-hydroxyphenyl-fluorone has been established (1) by determining, through acetylation, the number of hydroxyl groups present in the molecule; (2) by comparison of the monomethoxy- and dimethoxy-derivatives of our condensation product with the similar derivatives of *p*-hydroxyphenyl-fluorone that had been prepared by means of the Grignard reaction; (3) finally, by comparing the product with the compound which was definitely known, from the manner of its synthesis, to possess the constitution of *p*-hydroxyphenyl-fluorone.

p-Acetoxyphenyl-fluorone and *p*-Acetoxyphenyl-3-acetoxy-xanthenol.—



To 5 g. of hydroxy-fluorone was added 50 cc. of acetic anhydride and 2 cc. of sulfuric acid, care being taken to keep the solution cold. After two days, the mixture was poured into water and the precipitated mass was washed with alkali and water. The

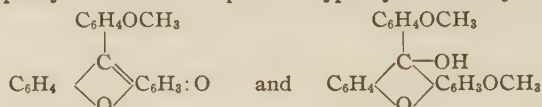
¹⁴ Gomberg and West, *J. Am. Chem. Soc.*, **34**, 1538 (1912).

dry, yellow product was allowed to stand in contact with ether, whereupon the diacetyl derivative dissolved. The mono-acetyl compound was obtained crystalline and pure from its concentrated solution in benzene by adding a large volume of ether. It melts at 204–205°. The diacetyl compound was obtained also in white crystals by adding to its solution in benzene a large volume of carbon disulfide; m. p., 138–140°.

Anal. Mono-acetyl compound. Calcd. for $C_{21}H_{14}O_4$: C, 76.34; H, 4.27. Found: C, 76.21; H, 4.30.

Diacetyl compound. Calcd. for $C_{23}H_{18}O_6$: C, 70.75; H, 4.64; acetic acid, 30.77. Found: C, 70.40; H, 4.65; acetic acid, 29.71.

p-Methoxyphenyl-fluorone and *p*-Methoxyphenyl-3-methoxy-xanthenol.—



When hydroxyphenyl-fluorone is methylated by means of methyl sulfate it takes up one or two methyl groups, depending upon the conditions of the experiment. When the methylation is carried out at room temperature in aqueous 4% sodium hydroxide solution, methoxyphenyl-fluorone, which is the first product of the reaction, precipitates and consequently further action of methyl sulfate is greatly retarded. However, when 50% acetone solution is employed, the methylation proceeds to the end and the dimethoxy derivative is the result.

The monomethoxy derivative was crystallized from benzene and from acetone and the orange-colored crystals melted at 206–208°.

Anal. Calcd. for $C_{20}H_{14}O_3$: C, 79.47; H, 4.67. Found: C, 79.69; H, 4.77.

The compound described proved to be identical in every way with the *p*-methoxyphenyl-fluorone prepared by Grignard's reaction from 3-hydroxyxanthone¹⁵ and *p*-anisylmagnesium iodide.

The dimethoxy derivative, recrystallized from alcohol and then from benzene, melted at 112–114°.

Anal. Calcd. for $C_{21}H_{18}O_4$: C, 77.47; H, 10.76. Found: C, 77.51; H, 10.79.

For purposes of comparison with our condensation product, the same dimethoxy compound was prepared from 3-methoxyxanthone¹⁶ and *p*-anisylmagnesium iodide. This, like our product from the condensation reaction, melted at 112–113°. The two on treatment with acetyl chloride gave identical, colored carbinolchloride-hydrochlorides melting at 120–122°.

Synthesis of *p*-Hydroxyphenyl-fluorone.—The *p*-methoxyphenyl-fluorone, prepared by Grignard's reaction as described above, was demethylated by aluminum chloride in antimony trichloride as the solvent. After purification, the product proved to be identical in every respect with the compound obtained in the condensation reaction. It melted at 285–295° with the evolution of phenol.

Oxidation by Air and Alkali.—A solution of 10 g. of *p*-hydroxyphenyl-fluorone in 100 cc. of 5% sodium hydroxide solution was warmed on the steam-bath for 12 hours. Upon neutralization of the solution, 6 g. of *o,p'*-dihydroxybenzophenone separated. This was recrystallized from benzene and melted then at 150–151°. Michael gives the melting point as 143–144°, Pfeiffer as 147–148° and Baeyer as 150–152°.¹⁷

¹⁵ (a) Baeyer, *Ann.*, **372**, 100 (1910). (b) Ullmann and Denzler, *Ber.*, **39**, 4335 (1906).

¹⁶ Ref. 15 a. Ref. 14, p. 1559.

¹⁷ (a) Michael, *Am. Chem. J.*, **5**, 83 (1883). (b) Pfeiffer, *Ann.*, **398**, 167 (1913). (c) Baeyer, *Ann.*, **354**, 177 (1907).

For further identification, the ketone was acetylated and the acetyl derivative melted at 89–90°, while Michael gives the melting point as 84–85°, and Dimroth and Zoeppritz as 120°. ¹⁸

This may be considered as a practical method for the preparation of *o,p'*-dihydroxybenzophenone, since the fluorone from which it is obtained is now itself readily accessible.

The Oxalic Acid Method for the Preparation of Aurin

By following the procedure as given by Zulkowski, ¹⁹ the yield of the crude reaction product was about 40%, based upon the amount of phenol used. The crude mixture was separated into its components according to the scheme outlined on p. 201 of this paper. The results are given below in Col. 1; parallel with these figures, in Col. 2, are reproduced Zulkowski's data

I		II	
Aurin	85%	Aurin	55%
Leuco-aurin	} 15%	" α -Aurin-oxide"	} 45%
Dihydroxybenzophenone		" β -Aurin-oxide"	
<i>p</i> -Hydroxyphenyl-xanthane		"Product 1"	
<i>p</i> -Hydroxyphenyl-fluorone		"Product 2"	

The yield of pure aurin by this method is almost exactly the same as that by the carbon tetrachloride method, namely, about 31–33% based upon the amount of phenol used in the reaction. Although the amount of by-products by the oxalic acid method is less than that obtained by the carbon tetrachloride method, the former method, on the other hand, requires the use of a large excess of oxalic acid; and as regards the by-products in the second method, the separation of pure aurin from these entails no difficulty.

The Composition of Several Technical Samples of Aurin

These samples were obtained from various sources and analyzed as to their contents according to our scheme of separation. In addition to aurin, they were found to contain leuco-aurin, *p*-hydroxyphenyl-fluorone, *p*-hydroxyphenyl-xanthane, di-*p*-hydroxybenzophenone and some unidentified material. The material from the Eastman Kodak Company (aurin) contained 55% of aurin; that from Merck and Company (aurin) contained 44%; that from the Schuchardt Chemical Company (corallin) contained 32%; and that supplied by Grüber and Company (corallin) contained 35%.

This investigation was made with the assistance of the National Aniline and Chemical Company Fellowship. We wish to express our obligations for the generous aid we have thus received.

¹⁸ (a) Ref. 17 a, p. 87. (b) Dimroth and Zoeppritz, *Ber.*, **35**, 992 (1902).

¹⁹ Zulkowski, *Monatsh.*, **16**, 358 (1895).

Summary

1. The condensation reaction between carbon tetrachloride and phenol has been investigated in detail. Eight of the nine products formed have been identified, and this made it possible to give an interpretation as to the mechanism of the condensation reaction.

2. Aurin is the chief product formed. Methods have been worked out for obtaining it quite pure, and a number of new derivatives of aurin have been prepared.

3. In addition to aurin, the following substances were isolated from the condensation mixture: leuco-aurin, *o,p',p''*-trihydroxytriphenyl carbinol, *p*-hydroxyphenyl-fluorone, *p*-hydroxyphenyl-xanthane, diphenyl carbonate, di-*p*-hydroxybenzophenone and *o,p'*-dihydroxybenzophenone.

4. It is possible to alter the conditions in the process of the condensation reaction in such a manner that, instead of aurin, diphenyl carbonate or di-*p*-hydroxybenzophenone becomes the chief product of the reaction. This procedure furnishes excellent preparative methods for these two substances. The decomposition of *p*-hydroxyphenyl-fluorone by alkali and air furnishes a very good method of preparing *o,p'*-dihydroxybenzophenone.

5. Aurin and its derivatives, such as the triacetyl and tribenzoyl carbinol, possess in a notable degree "residual affinity," and they give rise to many loosely bound combinations with alcohol, ether, ketones, carbon tetrachloride, aromatic hydrocarbons, etc.

6. It was found that the method hitherto employed for making aurin—namely, from phenol and oxalic acid—gives less by-products than the carbon tetrachloride method, but furnishes no better yields and is wasteful because it requires the use of a large excess of oxalic acid.

